

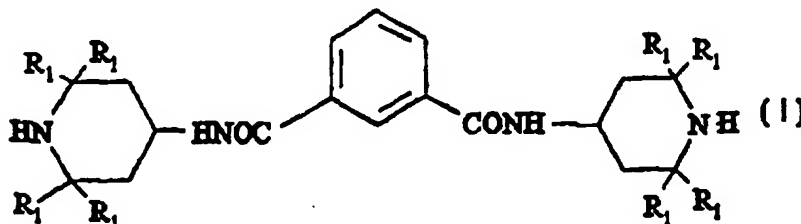


## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08K 5/3435, C08L 77/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/43335</b> <b>(43) International Publication Date:</b> 20 November 1997 (20.11.97)
<b>(21) International Application Number:</b> PCT/IB97/00533 <b>(22) International Filing Date:</b> 9 May 1997 (09.05.97)  <b>(30) Priority Data:</b> 9609742.3                      10 May 1996 (10.05.96)                      GB  <b>(71) Applicant (for all designated States except US):</b> CLARIANT FINANCE (BVI) LIMITED [-/-]; Citco Building, Wickhams Cay, P.O. Box 662, Road Town, Tortola (VG).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> KAUL, Bansi, Lal [CH/CH]; Bruckackerstrasse 48, CH-4105 Biel-Benken (CH).  <b>(74) Agents:</b> D'HAEMER, Jan et al.; Clariant International Ltd., Rothausstrasse 61, CH-4132 Muttenz (CH).		<b>(81) Designated States:</b> JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** IMPROVEMENTS IN OR RELATING TO ORGANIC POLYAMIDE COMPOUNDS**(57) Abstract**

A process of increasing the heat stability, light stability, chemical stability and dye affinity of synthetic polyamides as well as the stability and the light resistance of the coloring agents in the dyed or pigmented synthetic polyamides by adding thereto an additive having formula (I) wherein R<sub>1</sub> represents a methyl group as such or in the form of a stabilizer masterbatch composition. A stabilizer masterbatch composition according to the invention comprises a compound of formula (I) and a carrier polymer and is characterized by being transparent. A stabilizer and colorant masterbatch composition comprise in addition a colorant, i.e. a dyestuff or pigment. The invention also relates to modified synthetic polyamides obtainable by the aforementioned process having improved properties due to the stabilization effect of the compound of formula (I).



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

**IMPROVEMENTS IN OR RELATING TO ORGANIC POLYAMIDE COMPOUNDS**

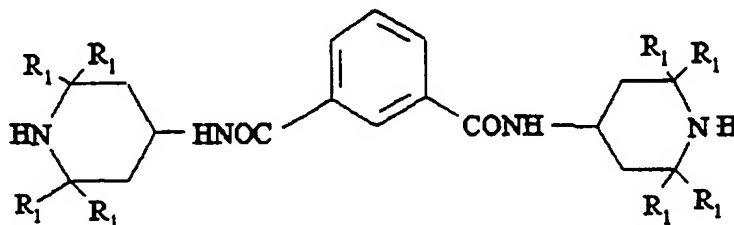
This invention relates to a process of increasing the heat stability, light stability, chemical stability and dyeability of synthetic polyamides as well as the stability and the light resistance of the colorants in dyed or pigmented synthetic polyamides. The invention also provides a process of improved dyeing or mass coloration of synthetic polyamides. The invention also relates to a stabilizer masterbatch composition as well as to modified polyamides obtainable by an aforementioned process.

Synthetic polyamides are in general worked, in particular during spinning processes, at temperatures of the order of 270°C or above. At these temperatures there are problems with the heat stability of synthetic polyamides. This can have serious consequences if, during spinning of synthetic polyamide, the through-put of the polymer is disrupted such that the polymer is exposed to the high temperatures of the spinning apparatus for longer periods than would be expected under normal running of the apparatus. Under such circumstances, there is an increasing likelihood of the synthetic polyamide thermally degrading. Further deficiencies of polyamides are their poor light stability, their poor melt processing stability due to their susceptibility to oxidation, their poor thermal-aging and oxidative chemical stability as well as their highly reducing polymer melts, limiting the suitability of colorants and additives, particularly in melt processing. Photodegradation is sometimes further accentuated in the case of colored materials due to the damage caused to the substrates in the dyeing processes and/or the phototendering influence of certain dyes.

It is the object of the present invention to provide a unique stabilizer specially tailored for use in polyamides to overcome the above-mentioned short-comings.

This object is achieved with a multifunctional compound as hereinunder defined containing groups bearing sterically hindered nitrogen atoms. It imparts photo and oxidative thermal/chemical stabilities to the substrates and the colorants applied thereto. It also enhances the dye affinity for pre-metallized as well as metal-free acid dyes.

The invention provides in one of its aspects a method of increasing the heat-stability, light stability, chemical stability and dye affinity of synthetic polyamide and in particular pigmented and/or filled synthetic polyamide by mixing therewith an effective amount of an additive according to the formula (I)



wherein R<sub>1</sub> represents a methyl group.

By adding an effective amount of the additive hereinabove described to synthetic polyamide one is able to increase the heat-stability, light stability, chemical stability and dye affinity of the polymer as well as the stability and the light resistance of the coloring agent in the dyed or pigmented polyamide without affecting certain desirable physical characteristics of the polymer, for example the relative viscosity and the degree of polymerization. Furthermore, the synthetic polyamide exhibits a decreased tendency to yellow and has improved stretchability and tensile strength.

The invention provides in another one of its aspects a method of improving the coloring of synthetic polyamides in the mass by mixing together a synthetic polyamide, a suitable dyestuff or pigment and an additive according to formula (I) as defined above.

The additive according to formula (I) may be present in the synthetic polyamide in amounts of from 0.1 to 5.0%, preferably 0.1 to 2.0% by weight based on the total weight of the heat-stabilized synthetic polyamide.

The polyamide to be stabilized can be a homopolyamide, a copolyamide, a mixture or blend of polyamides or of a polyamide and another polymer.

Preference is given to homopolyamides and/or copolyamides made from  $\omega$ -aminocaproic acid,  $\omega$ -aminoenanthoic acid,  $\omega$ -aminocaprylic acid,  $\omega$ -aminopelargonic acid,  $\omega$ -aminocapric acid,  $\omega$ -aminoundecanoic acid,  $\omega$ -aminolauric acid, caprolactam, lactam-7, lactam-8, lactam-9, lactam-10, lactam-11 and/or laurolactam.

The polyamides to be stabilized can also be selected from the group of polyamides made, for example from dimethylenediamine, trimethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, polyetherdiamine and mixtures thereof on the one hand, and oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, nonedicarboxylic acid, decanedicarboxylic acid, undecanedioic acid, dodecanedioic acid, dimerised fatty acids and mixtures thereof on the other hand.

The preparation of the synthetic polyamides stabilized according to the invention can be effected by conventional means, preferably by mixing the additive of formula (I) with molten synthetic polyamide in a suitable receptacle, for example in an extruder prior to molding or spinning or before or during the polycondensation process of the synthetic polyamide itself.

Synthetic polyamides used in the invention are preferably dyed or pigmented, for example by topical application or by application in the melt in accordance with conventional methodology. Any type of dyestuff or pigment is suitable provided that it is stable at the high temperatures encountered in the melt. Preferred dyestuffs are monoazo complexes, in particular, the chromium complexes that are sufficiently stable at the high working temperatures encountered in, e.g. a spinning process. Preferred reactive dyestuffs are those halogen-containing triazinyl or vinyl group-containing metallized azo dyestuffs, in particular, those metallized with chromium, nickel or copper. Preferred pigments are, for example Pigment Yellow 192, Pigment Orange 68 and Pigment Red 149. Preferred polymer soluble dyes are for example Solvent Red 179.

If dyestuffs or pigments are employed in the synthetic polyamides they are preferably employed in amounts of from 0.1 to 10 parts, more preferably, 0.1 to 4 parts per 100 parts of the synthetic polyamide.

Synthetic polyamides may additionally comprise fillers or fibres, for example glass spheres or glass fibres, and/or delusterants, for example titanium dioxide which may be present in proportions of from 0.1 to 5 parts, more preferably 0.2 to 2.0 parts, e.g. 0.2 parts per 100 parts of polyamide.

The invention provides in another one of its aspects a stabilizer masterbatch composition which is transparent. Stabilizer masterbatch compositions according to the invention comprise 10 to 80% by weight, preferably 5 to 50% by weight, more preferably 15 to 40% by weight of the compound of formula (I) and 90 to 20% by weight, preferably 95 to 50% by weight, more preferably 85 to 60% by weight of a thermoplastic carrier polymer which is identical to or compatible with the polyamide to be stabilized.

A masterbatch composition may comprise in addition to the additive according to the invention a coloring agent. In this case such compositions comprise 2.5 to 40% by weight, preferably 5 to 25% by weight of the compound of formula (I), 5 to 40% by weight, preferably 7.5 to 20% by weight of a suitable dye or pigment and 95 to 50% by weight, preferably 85 to 60% by weight of the afore-mentioned carrier polymer.

The invention provides in a further one of its aspects a modified synthetic polyamide obtainable by the process hereinabove defined which polyamide having improved heat stability, light stability, chemical stability and dye affinity and in the case of a dyed or pigmented polyamide also having improved light resistance and stability of the colorant in said polyamide.

There now follow examples which are illustrative of the invention.

In the following examples all parts and percentages are by weight and all temperatures are given in degrees Celsius.

## **EXAMPLES**

### **I. Production of the yarn**

Polyamide 6 (BASF, type BS 703) or polyamide 6.6 chips (BASF, type AS 2503) are dried in a vacuum tumble drier for 8 hours at a temperature of 110° or 125°. 2 kg batches of the dried polymer are combined and milled for one hour with an appropriate amount of a compound of the formula (I) [which is used directly without any further drying as it is delivered predried] to form 0.5% or 1.0% mixtures of the compound in polymer. Filament yarns are melt-spun from the afore-mentioned mixtures under conditions as summarized in table 1 using the following equipment: An extruder fitted with one dynamic mixer at the top of the 30mm-screw and two static mixers before the spinning head. For winding of the filament yarns consisting of 32 filaments a BARMAG SW46 winder is used together with two godets. The as-spun yarns are drawn subsequently on an DIENES draw-twisting machine to reach a residual elongation of  $\pm 25\%$ . The applied drawing ratios are given in table 2.

### **II. Test methods**

For analytical characterization of as-spun and drawn yarns different physical and chemical methods are applied:

- tenacity/elongation/initial modulus
- sonic modulus
- uster unevenness
- solution viscosity.

**a) Mechanical properties**

The mechanical properties are determined with the Statimat M from TEXTTECHNO, the fiber mass fluctuation is measured with the Uster Tester III from ZELLWEGER Uster and the sonic modulus is calculated from the results of determination of sound velocity measured with the Dynamic Modulus Tester PPM-5R from MORGAN Co., Inc.

**b) Viscosity**

The solution viscosity is determined with an Ubbelohde type viscometer and the viscosity values are given as reduced specific viscosity.

**c) Light stability**

Light fastness tests are carried out on a Xenotest where the drawn fibers are reeled around the metal frames, fixed on an carousel and exposed to light for 50, 100 and 200 hours in total. After these periods of time tenacity and initial modulus are measured again and compared to the corresponding sample, which has not been exposed to light.

**d) Dyeing and color matching**

The drawn yarns formed according to the process described above are knitted on a round knitting machine from LUCAS to provide test samples for dyeing. In case of processing those as-spun yarns of 50 dtex, two threads were combined before knitting to reach a comparably dense fabric as for the higher counts of 100 dtex. The knitted stockings are heat set on a pad-steam device at a temperature of 100° and 95% relative humidity for a period of 20 minutes. Thereafter test samples are dyed on a MATHIS Labor JET with NYLOSAN Dyes (CLARIANT) using two different kind of dyestuff.



**TABLE I**

Extruder and winder settings

**PA6 settings**

test no.	additive %	extruder zone 1-2	extruder zone 3-5	temperatures (°C) mixer	spinning head temp. (°C) top	spinning head temp. (°C) bottom	melt	screw rpm	pressure bar	me. pum rpm	count dtex	SF conc. %	SF pum	godets m/min	rav. freq. Hz	winder m/min
604/1	0.0	290	275	275	285	300	292	34	55	35.0	98.5	11.6	0.45	3990	200	4000
604/2	0.0	290	275	275	285	300	292	44	90	35.0	100.0	11.6	0.45	3990	200	4000
604/3	0.0	290	275	275	285	310	298	20	55	17.5	48.5	11.6	0.30	3998	200	4000
604/4	0.0	290	275	275	285	310	298	30	90	17.5	50.0	11.6	0.30	3975	200	4000
604/5	0.5	290	275	275	285	310	298	30	55	35.0	101.0	11.6	0.50	3980	200	4000
604/8	0.5	290	275	275	285	310	298	45	90	35.0	99.3	11.6	0.50	3980	200	4000
604/9	0.5	290	275	275	285	310	298	30	90	17.5	50.0	11.6	0.30	3985	200	4000
605/1	1.0	290	270	270	290	310	298	32	55	35.0	98.5	11.6	0.55	3985	200	4000
605/3	1.0	290	270	270	290	310	298	42	90	35.0	102.8	11.6	0.55	3985	200	4000
605/6	1.0	290	270	270	290	310	298	22	55	17.5	49.4	11.6	0.35	3978	200	4000
605/5	1.0	290	270	270	285	305	294	18	90	17.5	49.8	11.6	0.35	3978	200	4000

## Continuation of Table 1

## PA6.6 settings

test no.	additive %	extruder zone 1-2	temperatures (°C) zone 3-5	mixer	spinning head temp. (°C)		screw rpm	pressure bar	me.pum rpm	count dtex	SF conc. %	SF pum	godets m/min	trav.freq. Hz	winder m/min
612/1	0.0	290	280	280	290	300	298	44	35.0	100.6	11.6	0.50	4041	190	4000
612/3	0.0	290	280	280	290	300	298	54	35.0	100.3	11.6	0.50	4043	190	4000
612/5	0.0	290	280	280	290	300	298	37	17.5	49.8	11.6	0.40	4045	190	4000
612/7	0.0	290	280	280	290	295	296	45	17.5	50.5	11.6	0.40	4042	190	4000
612/15	0.5	290	280	280	290	295	296	60	35.0	113.7	11.6	0.50	4035	200	4000
612/8	0.5	290	280	280	290	295	296	62	35.0	101.0	11.6	0.50	4042	190	4000
612/11	0.5	290	280	280	290	295	296	38	17.5	57.1	11.6	0.40	4036	190	4000
612/14	0.5	290	280	280	290	295	296	50	17.5	57.9	11.6	0.40	4036	190	4000
612/21	1.0	290	280	280	290	295	296	56	35.0	116.0	11.6	0.50	4035	200	4000
612/24	1.0	290	280	280	290	295	296	70	35.0	113.5	11.6	0.55	4035	200	4000
612/19	1.0	290	280	280	290	295	296	39	17.5	57.5	11.6	0.40	4035	200	4000
612/17	1.0	290	280	280	290	295	296	58	17.5	57.7	11.6	0.40	4035	200	4000

**Type I**

(dyeable from weak acidic system)

- Nylosan Yellow F-L
- Nylosan Red F-GL
- Nylosan Blue F-L 150
- Nylosan Green F-BL 130

**Type II**

(dyeable from about neutral dyeing liquor)

- Nylosan Red F-2BLN250
- Nylosan Blue NFL 180
- Nylosan Brilliant Green F-6GLN
- Nylosan Red EBLN
- Nylosan Blue N-5GL200

according to the following method: A test sample is placed in a dyebath at 20° having a liquor ratio of 1:40 and consisting of 2% dyestuff, 0.5% Lyogen PAM and a sodium acetate/acetic acid buffer (pH 4.5) for dyes of the type I and a phosphate buffer (pH 6) for dyes of type II. The temperature is increased to 98° over a period of 45 minutes and the temperature maintained for a further 60 minutes. Thereafter, the temperature is reduced to 80° before flushing the dyes sample with cold water. The dyed samples are characterized by means of color matching with a Chroma-Meter CR 310 (MINOLTA) providing the CIELab values, which can be converted to  $\Delta E$ ,  $\Delta L$ ,  $\Delta C$  and  $\Delta H$  according to the definitions given in the German standard DIN 6174. As basic for calculation of the  $\Delta$ -values the correspondingly produced samples without the additive according to the invention are used as reference sample.

For reasons of comparison not only in relation to an unmodified polymer produced under the same conditions, also a commercial PA6- and PA6.6-fabric, respectively, is dyed and measured accordingly.

**e) Oxidative chemical stability tests**

To determine the influence of the additive according to the invention on the oxidative chemical stability of fibers, nylon fibers are also exposed to the peroxide soda boil bleaching conditions. Such treatments are a common practice to obtain a whiter yarn and/or during the cleaning of the materials in their life cycle.

**f) Oxidative thermal stability tests**

To determine the oxidative thermal stability, the fibers are subjected to oven test in air for one hour at 180°, 190° and 200°, and the changes in color and physical properties (relative viscosity, tenacity, modulus & elongation) are measured.

## **II. Test results**

### **1. Spinnability**

The spinnability of the polymers modified with the additive according to the invention is very good which is reflected in very stable pressure conditions in the extruder, a smooth fiber formation and a good package build up without fluffs.

### **2. Mechanical properties**

The test results are summarized in table 2.

The mechanical properties of the as-spun yarns are quite comparable to the reference yarns and especially for the PA6.6 polymers modified according to the invention in most cases even are markedly improved. In general for both polymers there is a tendency towards higher figures for tenacity, initial and sonic modulus with increasingly higher amounts of additive and decreased fiber count, respectively, while the variation of extruder pressure as expected has no significant effect on mechanical fiber properties. It is well known that reducing the filament count (dpf) under constant spinning conditions is due to higher degree of orientation during fiber formation, so that tenacity and moduli are improved.

Considering the drawn fibers these tendencies are still more pronounced compared to as-spun fibers. Again the fibers modified according to the invention show a remarkable increase in tenacity caused by the addition of 1% of the additive. For the modified PA6 fibers an increase of about 10% has to be stated, whereas in case of the

modified PA6.6 fibers this increase is even more than 10% of the tenacity of the not modified reference yarn.

As a general conclusion it can be stated that the addition of the additive of formula (I) according to the invention to polymers improves the fiber mechanical properties.

### **3) Light stability**

The test results are summarized in table 3a to 3d.

**TABLE 2**

Mechanical properties of as-spun and drawn yarns modified or unmodified with the additive according to the invention.

**PA6**

test no.	additive		extr. press. bar	count dtex	elongation %	tenacity cN/tex	modulus		Uster %	drawn yarn		
	%						initial cN/tex	sonic cN/tex		tenacity cN/tex	modulus cN/tex	draw ratio 1 : x
604/1	-		55 - 60	98.5	71.0	36.2	334.7	418.3	2.69	52.86	372	1.465
604/2	-		85 - 90	100.0	74.0	36.5	326.0	396.8	2.04	52.54	401	1.45
604/3	-		55 - 60	48.5	57.7	36.4	362.3	384.0	2.49	51.29	364	1.28
604/4	-		85 - 90	50.0	53.9	33.1	366.5	405.1	2.17	51.81	468	1.35
604/5	0.5		55 - 60	101.0	74.1	36.7	341.6	384.3	2.67	56.08	390	1.45
604/8	0.5		85 - 90	99.3	71.3	36.7	351.2	378.5	2.6	54.11	391	1.455
604/9	0.5		85 - 90	50.0	63.8	38.8	367.7	446.3	2.28	51.99	419	1.35
605/1	1		55 - 60	98.5	61.6	34.8	344.8	390.8	2.82	54.43	446	1.35
605/3	1		90	102.8	63.7	35.0	353.5	393.2	2.7	52.91	425	1.37
605/5	1		90	49.8	61.2	38.9	368.5	361.5	2.6	56.61	427	1.35
605/6	1		55	49.4	63.1	39.1	372.0	393.5	2.15	57.51	305	1.42

Continuation of Table 2

PA6.6

test no.	additive			extr. press.		count dtex	elongation		tenacity cN/tex	modulus		Uster %	tenacity		drawn yarn		draw ratio 1 : x
	%	bar					%			initial cN/tex	sonic cN/tex		cN/tex		modulus cN/tex		
612/1	-	55				100.6	90.1		26.1	290.8	347.3	2.7	41.35		379		1.58
612/3	-	90				100.3	88.8		26.8	296.2	343.8	2.81	43.99		373		1.6
612/5	-	55				49.8	82.6		30.0	344.9	418.7	3.37	44.74		367		1.52
612/7	-	90				50.5	73.1		28.0	331.6	368.8	2.1	41.35		339		1.58
612/15	0.5	55				113.7	86.3		32.5	307.7	401.5	1.96	50.79		426		1.56
612/10	0.5	90				100.0	85.6		27.0	305.3	377.0	2.07	48.62		399		1.59
612/11	0.5	55				57.1	86.1		33.1	316.0	333.6	2.3	52.03		455		1.56
612/14	0.5	90				57.9	81.6		33.1	326.4	374.7	2.37	49.59		328		1.56
612/21	1	55				116.0	85.4		28.1	279.1	390.9	2.28	49.07		410		1.56
612/24	1	90				113.5	86.6		29.6	288.2	399.1	2.11	47.48		329		1.54
612/19	1	55				57.5	80.8		33.2	340.4	380.4	2.02	50.58		388		1.5
612/17	1	90				57.7	76.7		32.5	338.6	388.6	2.21	50.65		401		1.52

**TABLE 3a - 3d**

Tenacity and initial modulus of PA6 and PA6.6 fibers modified or unmodified with the additive according to the invention after exposure to light

**a) Tenacity (cN/tex) of PA6 fibers, extruder pressure 50 bar**

time (h)	0	50	100	200
0%, 50dtex	51.3	48.6	45.8	38.4
0%, 100dtex	52.9	49.6	49.6	48.6
0.5%, 50dtex	-	-	-	-
0.5%, 100dtex	56.7	56.1	55.7	49.6
1%, 50dtex	57.5	49.6	56.4	47.9
1%, 100dtex	54.4	56.2	56.5	51.7

**b) Initial modulus (cN/tex) of PA6 fibers, extruder pressure 50 bar**

time (h)	0	50	100	200
0%, 50dtex	364	422	511	540
0%, 100dtex	372	489	500	497
0.5%, 50dtex	-	-	-	-
0.5%, 100dtex	390	508	549	563
1%, 50dtex	305	496	586	587
1%, 100dtex	446	558	587	583



**c) Tenacity (cN/tex) of PA6.6 fibers, extruder pressure 50 bar**

time (h)	0	50	100	200
0%, 50dtex	44.7	44.6	42.1	36.4
0%, 100dtex	41.4	40.3	39.4	34.5
0.5%, 50dtex	52.1	47.8	49.4	43.1
0.5%, 100dtex	50.8	49.7	49.2	47.5
1%, 50dtex	50.6	48.1	48.1	45.4
1%, 100dtex	49.1	45.6	45.4	41.4

**d) Initial modulus (cN/tex) of PA6.6 fibers, extruder pressure 50 bar**

time (h)	0	50	100	200
0%, 50dtex	367	449	483	506
0%, 100dtex	379	366	479	489
0.5%, 50dtex	455	519	550	503
0.5%, 100dtex	426	484	554	580
1%, 50dtex	388	483	525	550
1%, 100dtex	410	433	499	506

For all modified samples, light fastness is improved. Both measured parameters exhibit higher values for the modified samples. That means, the level of light fastness is shifted about 10 - 20% towards higher tenacity or initial modulus by the addition of the additive according to the invention. Furthermore, a higher percentage of the additive leads to higher values of mechanical data. In the same way tenacity and modulus are influenced by the filament count, as the 100 dtex fibers always show higher values than the lower count fibers.

In general, the addition of the additive according to the invention to polymers improves the light fastness with respect to the fiber-mechanical properties.

#### 4. Oxidative chemical stability

The results of the influence of the additive according to the invention on the chemical degradation of PA6.6 fibres are summarized in table 4.

**TABLE 4**

Normalized Tenacity of PA6.6 fibers modified or unmodified with the additive according to the invention before and after exposure to peroxide soda boil bleaching conditions

Normalised tenacity (cN/tex) of PA6.6 fibers (50dtex), extruder pressure 50bars.

Additive (%)	Non-Bleached	Bleached
0.0	94.7	49.8
0.5	100.0	75.6
1.0	100.0	78.0

Here again an improvement in the stability as a result of the incorporation of the additive according to the invention is observed.

#### 5. Heat stability

The test results of the influence of the additive according to the invention on the thermal stability of PA6 and PA6.6 (100dtex/55bars) fibres are summarized in table

**TABLE 5a**

Absorbance, normalised viscosity, normalised tenacity, modulus of PA6 fibers unmodified or modified with the additive according to the invention.

Treatment Temp. (°C)	Absorbance at 390 nm	
	0% Additive	0.5% Additive
180	0.231	0.032
190	0.294	0.134
200	0.399	0.084

Treatment Temp. (°C)	Normalised Viscosity (%)	
	0% Additive	0.5% Additive
180	74.34	94.67
190	72.8	90.99
200	71.47	87.62

Treatment Temp. (°C)	Normalised Tenacity (%)	
	0% Additive	0.5% Additive
180	66.04	89.25
190	60.66	63.49
200	32.36	35.47

Treatment Temp. (°C)	Modulus (%)	
	0% Additive	0.5% Additive
180	87.19	109.64
190	79.71	103.8
200	66.57	86.46

**TABLE 5b**

Absorbance, normalised viscosity, normalised tenacity and energy at break of PA6.6 fibers unmodified or modified with the additive according to the invention.

Treatment Temp. (°C)	Absorbance at 390 nm		
	0% Additive	0.5% Additive	1% Additive
180	0.3612	0.312	0.3054
190	0.4603	0.3463	0.339
200	0.6535	0.4242	0.4032

Treatment Temp. (°C)	Normalised Viscosity (%)		
	0% Additive	0.5% Additive	1% Additive
180	21.9	53.5	59.1
190	19.0	45.3	52.4
200	19.7	38.4	42.8

Treatment Temp. (°C)	Normalised Tenacity (%)		
	0% Additive	0.5% Additive	1% Additive
180	37.0	54.5	65.5
190	33.0	47.3	60.5
200	30.0	41.0	59.1

Treatment Temp. (°C)	Energy at break (mJ)		
	0% Additive	0.5% Additive	1% Additive
180	0.103	2.196	2.278
190	0.093	1.081	1.155
200	0.074	0.502	0.682

The protection granted to the fibers by the additive according to the invention versus unmodified fibers is very conspicuous both regarding discoloration and degradation of the mechanical properties.

**6. Dyeability**

The dyeing properties of the drawn fibers are determined using both pre-metallized and metal-free acid dyes. The improvements in overall properties are even more pronounced in the case of pre-metallized dyes. The results are summarized in table 6.

**TABLE 6**

Influence of the additive according to the invention on the dyeability of PA6.6 fibers

	Color change (DE) of PA6.6 fibers (50dtex/55bars)	
	0.5% Additive	1% Additive
Nylosan Red F-GL	1.98	2.78
Nylosan Blue NFL 180%	1.54	2.41
Nylosan Yellow F-L	2.97	3.69
Nylosan Red EBNL	3.69	2.95

extr. press (bar)	Color Strenght (%) of Nylosan Blue NFL 180%		
	count (dtex)	0.5% Additive	1% Additive
55	100	119.0	120.5
90	100	101.8	121.2
55	50	118.0	135.4
90	50	118.5	119.8

It can be seen that even in 2% dye concentration, the fibers show deeper and stronger shades with increasing amounts of the additive according to the invention.

Deeper and stronger shades with same amount of dye also mean better ecology in dye houses due to the less amount of dye in the effluent water.

The deeper dyeability imparted to the fibers by the application of the additive according to the invention is further confirmed by tests where the fibers are dyed for 24 hours to saturation limits and the dye uptake is determined by reextraction of the dyes with aqueous dimethyl formamide followed by optical density measurements. The test results are summarized in table 7.

**TABLE 7**

Influence of the additive according to the invention on the dyeability of PA6 and PA6.6 fibers with the dye POLAR BLUE RAWL

**Concentration of Dye on Fibre (%)**

Additive (%)	Nylon 6	Nylon 6.6
0.0	1.9	1.8
0.5	2.8	2.6
1.0	3.8	3.4

This experiment not only underlines the deeper dyeability of the fibers modified with the additive according to the invention, but also provides an evidence that the compound of formula (I) does not get extracted out of the fibers even after subjecting the corresponding fibers to extreme dyeing conditions.

**7. Light fastness of the dyeings**

In table 8 the results of the light fastness of the additive containing dyeings versus untreated dyeings are summarized. There is a dramatic improvement in the dye-light fastness.

**TABLE 8**

Influence of the additive according to the invention on dye-light fastness of PA6.6 dyed fibers (100 dtex/55bars)

**Blue Scale Note**

Additive (%)	Nylosan Blue NFL 180%	Nylosan Red EBNL	Nylosan Yellow F-L
0.0	5.5	3.5	5.0
0.5	6.5	6.0	6.0
1.0	7.0	7.0	7.0

The additive according to the invention is also tested in carpet fibers. In table 9 the results of the heat and light stability tests of carpet fibers modified with the compound of formula (I) are summarized.



Treatment Temp. (°C)	Normalised Tensile Strenght (%)	
	0% Additive	0.5% Additive
180	100.0	100.0
190	33.3	86.9
200	22.3	78.0

Treatment Temp. (°C)	Normalised Modulus (%)	
	0% Additive	0.5% Additive
180	100.0	109.6
190	87.8	97.2
200	87.0	93.9

It can be seen that even at 0.25% concentration of the additive according to the invention a dramatic stability is granted to the fibers.

In proof of advanced performance characteristics imparted to nylon fibers using the additive according to the invention PA6 carpet fibers of 1300 dtex/68 filaments are produced with and without the additive according to the invention. The resulting fibers are dyed in five trichromic shades. The dyeings are then exposed to four cycles of FAKRA. The fibers not containing any additive not only faded but also degraded. Even parts of the fibers not exposed to light but only to the heat in the FAKRA test also faded and are degraded. Whereas the fibers containing the additive according to the invention are almost unaltered and also show much deeper shades with same concentration of dyes in dyebaths.

The compound of formula (I) is also tested in nylon engineering polymers. The test results are summarized in table 10.

#### **TABLE 10**

Influence of the additive according to the invention on the light stability of poly(ether-bloc-amide) plates after 1000 hours light exposure (CAM 7).

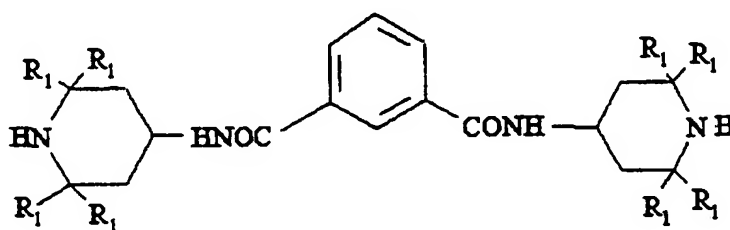
**Transparency (%)**

Additive	Before Exposure	After Exposure
No Additive	89.4	1.5
0.2%Irganox 1098	89.8	2.2
0.6% Sanduvor 3944	89.9	22.1
0.6% Sanduvor PR31	89.8	48.6
Additive according to formula I (R1 = Methyl)	90.7	83.2
0.6% Sanduvor VSU	90.0	2.7
0.3% Sanduvor VSU + 0.3% Sanduvor 3944	90.6	11.4
0.3% Sanduvor VSU + 0.3% Sanduvor PR31	90.7	33.5
0.3% Additive according to formula I (R1 = Methyl) + 0.3% Sanduvor VSU	89.3	77.9

As in fibers, the additive according to the invention also improves heat and light stability and retention of transparency on exposure to light.

**CLAIMS**

1. A process of increasing the heat stability, light stability, chemical stability and dye affinity of synthetic polyamides as well as the stability and the light resistance of the coloring agents in the dyed or pigmented synthetic polyamides comprising incorporating therein before or during processing an effective amount of a compound of formula (I) as such or in the form of a masterbatch composition according to claim 5 or claim 6,



wherein R<sub>1</sub> represents a methyl group.

2. A process according to claim 1 wherein the compound of formula (I) is added in an amount of from 0.1 to 5.0 parts by weight per 100 parts by weight of the synthetic polyamide.
3. A process of improving the coloring of synthetic polyamides in the mass by mixing together a synthetic polyamide, a suitable dyestuff or pigment as such or in the form of a colorant masterbatch composition and a compound of formula (I) as defined in claim 1 as such or in the form of a stabilizer masterbatch composition according to claim 5.
4. A process according to claim 1 or claim 3 wherein the polyamide is a homopolyamide, a copolyamide, a mixture or blend of polyamides or of a polyamide and another polymer.

5. A stabilizer masterbatch composition, particularly according to claim 1 or claim 3 comprising a compound of formula (I) as defined in claim 1 and a carrier polymer which is identical to or compatible with the polyamide to be stabilized characterized by being transparent.
6. A stabilizer and colorant masterbatch composition according to claim 3 comprising a compound of formula (I) as defined in claim 1, a coloring agent and a carrier polymer which is identical to or compatible with the polyamide to be stabilized.
7. A modified synthetic polyamide obtainable by a process according to claim 1 or claim 3 and any article manufactured therefrom.
8. The use of an additive according to the formula (I) as a heat, light, chemical and color stabilizer as well as a dye affinity enhancer in a synthetic polyamide.

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 C08K5/3435 C08L77/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 095, no. 005, 30 June 1995 & JP 07 033738 A (MITSUBISHI KASEI CORP), 3 February 1995, see abstract	1
A X	EP 0 379 470 A (SANDOZ) 25 July 1990 see page 4, line 40 - line 45 see page 8, line 3 - line 8 see page 10, line 33 - line 40 see page 40, line 1 - line 7; claims 1,2,4 --- -/--	1,3,8 1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*A\* document member of the same patent family

Date of the actual completion of the international search

18 August 1997

Date of mailing of the international search report

03.09.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Engel, S

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	<p>JP 09 041 217 A (TEIJIN LTD.) 10 February 1997 see page 4; figure C &amp; DATABASE WPI Section Ch, Week 9716 Derwent Publications Ltd., London, GB; Class A23, AN 97-176165 &amp; JP 09 041 217 A (TEIJIN LTD) , 10 February 1997 see abstract</p> <p>-----</p>	1,2



Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 379470 A	25-07-90	DE 3901716 A	26-07-90
		DE 3901717 A	26-07-90
		DE 3930089 A	21-03-91
		DE 69025963 D	25-04-96
		DE 69025963 T	21-11-96
		EP 0618256 A	05-10-94
		ES 2087141 T	16-07-96
		JP 2265966 A	30-10-90
		CN 1045109 A,B	05-09-90
		DE 69007092 D	07-04-94
		DE 69007092 T	21-07-94
		WO 9103511 A	21-03-91
		EP 0461206 A	18-12-91
		HK 34797 A	27-03-97
		JP 4501881 T	02-04-92
		US 5470921 A	28-11-95
-----			
JP 9041217 A	10-02-97	NONE	
-----			